Oxo-peroxo vanadates(v): Synthesis, characterisation and uses in catalytic oxidation reactions

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The reaction of V_2O_5 with H_2O_2 in a neutral medium can be utilised for the generation of an unknown and presumably binuclear oxo-bridged peroxovanadate(v), $(PPh_4)_2[V_2O_2(\mu_2\text{-}O)(\mu_2\text{-}O_2)(\eta_2\text{-}O_2)_2]$ containing two triangular and one bridging peroxo group. The compound undergoes stoichiometric oxygen transfer reaction with Ph_3P and methyl benzenes such as toluene, *o*- and *p*-xylenes and the binuclear complex gets converted to $A_4[VO_4]$. The compound furnishes catalytic oxidation reaction with methyl benzenes in presence of hydrogen peroxide to yield benzoic acid from toluene and *o*- and *p*-toluic acids from *o*- and *p*-xylenes respectively. The reaction probably goes via a radical mechanism. The crystal of binuclear vanadium complex fastly loses its lustre and becomes unsuitable for X-ray diffraction. Even at low temperature the lustrous crystals are vulnerable towards X-radiation.

Keywords: Peroxo, methyl benzenes, binuclear.

Introduction

The reaction of V_2O_5 with H_2O_2 is very complicated and different types of compounds are formed depending on the pH of the medium. Subsequent researches in this area[1] suggested that the addition of H_2O_2 to V_2O_5 produced a red colour believed to be due to the formation of a monomeric monoperoxovanadate(v) cation $[VO(O_2)]^+$. The red colour thus obtained is stable in moderately acid medium. In an excess of H_2O_2 the red cation is converted to yellow oxodiperoxovanadate(v) anion[2] $[VO(O_2)_2]^{2-}$. It was concluded from previous studies in solution that the number of peroxo groups per V atom increases with increased alkalinity and decreases with increased acidity of the medium. Reactivity investigations of vanadium in both aqueous and nonaqueous media has been the central theme of a number of studies. Vanadium(v) peroxo complexes are less studied with regard to their oxidising properties due to their less efficiency[3] but they are highly selective than Mo(v) peroxo complexes[4]. H_2O_2 being a readily available oxidant is used as an oxidising agent for this purpose. The mild oxidising action of H_2O_2 is considerably enhanced in the presence of certain metal catalysts[5]. The intention of selecting methyl benzenes as substrates is due to their ample availability as raw materials from coal and petroleum processing industries. Generally the first row transition metal complexes prefer homolytic oxidations involving free radical intermediates characterised by one electron oxidation-reduction steps of the metals. The hydrocarbon substrate is generally not coordinated to the metal and is oxidised outside the coordination sphere[6]. Consequently the oxidation is not very selective and does not preserve the stereochemical configuration of the substrate.

The oxidation of aromatic hydrocarbons[7] like toluene is a difficult task, no doubt, but the oxidation of xylenes to the corresponding dicarboxylic acids is even more difficult, because the methyl group in the intermediate *ortho*- or *para*-toluic acid is deactivated by the electron withdrawing carboxyl group and is particularly resistant to further oxidation. Though the reactivity of vanadium(v) peroxo compound is suppressed to some extent, yet the selectivity has been intact and *o*- and *p*-toluic acids have been obtained from *o*- and *p*-xylenes respectively.

Experimental

Preparation and purification of complexes:

Di (tetraphenylphosphonium) dioxo-μ_2-oxo-μ_2 peroxo bis(η^2-peroxo) divanadate(v).

$(PPh_4)_2[V_2O_2(\mu_2\text{-}O)(\mu_2\text{-}O_2)(\eta^2\text{-}O_2)_2]$:
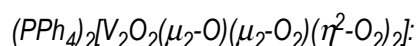
V_2O_5 (0.25 g; 1.37 mmol) was dissolved in 30% H_2O_2 (25 ml) with constant stirring when a vigorous reaction took place with evolution of O_2 and the original yellow colour of the solution changed to reddish orange and finally a brick red solid mass separated out. The reaction mixture was then cooled and a further addition of 30% H_2O_2 under stirring affords an orange yellow homogeneous solution. This solution was stable for 2–3 h. Addition of an aqueous ethanol (1:1) solution (15 ml) of PPh_4Cl (1.03 g) gave an orange brown compound **(1)**, yield 75%. This was filtered off, washed with water and ethyl alcohol and finally with diethyl ether and dried over $CaCl_2$ *in vacuo.* The results of elemental analysis of C, H, P, V is given in Table 1.

Table 1

	Found	Calculated
C	62.0	62.3
H	4.42	4.36
P	6.59	6.59
V	11.0	11.0

Stoichiometric oxidations by 1

To an acetonitrile solution (30 ml) of the compound (0.14 g, 15 mmol), PPh_3 (0.08 g, 0.30 mmol) in acetonitrile (10 ml) was added and the reaction mixture was refluxed for 2–3 h when the solution became deep green in colour. The green solution was then evaporated and the solid mass obtained by evaporation was extracted with diethyl ether. The insoluble part left after the ether extraction (the ether extract gave Ph_3PO) was washed with water, 95% ethanol and finally with diethyl ether and dried over $CaCl_2$ *in vacuo.* The compound was then crystallised from acetonitrile/pentane/dietylether (1:2:3) when deep green microcrystalline compound separated out, yield was 0.12 g (55%). The product was identified as hitherto unknown ($PPh_4)_4[VO_4]$ **(2)**. The elemental analysis of the compound is given in Table 2.

Table 2

	Found	Calculated for $C_{96}H_{80}P_4O_4V$
C	77.5	78.3
H	5.52	5.47
P	8.36	8.41
V	3.39	3.46

Oxidation of toluene:

To a methanol solution (25 ml) of the compound (0.14 g; 0.15 mmol) 5 ml methanol solution of toluene (0.014 g; 0.15 mmol) was added and the mixture was refluxed for 3–4 h. The solution was cooled, evaporated to dryness and the solid mass left was extracted with ether to get a colourless solution and a green solid mass was left as residue (0.089 g; 57%). The ether extract was further extracted with aqueous sodium bicarbonate, and the aqueous extract was acidified to obtain white shinning crystals of benzoic acid (0.016 g; 87%). The identity of the acid was confirmed by undepressed mixed melting point and superimposiblity of IR spectra with authentic benzoic acid. The green microcrystalline solid was analysed and characterised as $(PPh_4)_4[VO_4]$.

Oxidation of o-xylene and p-xylene:

Similar to the method described above, a methanol solution (25 ml) of the compound (0.014 g; 0.15 mmol), and *o*-xylene (0.016 g; 0.15 mmol)/*p*-xylene (0.016 g; 0.15 mmol) was mixed separately and refluxed for 3–4 h the solution was cooled, evaporated nearly to dryness and diethyl ether added to the nearly dry mass. From this mixture a green mass remained as residue (in both the cases) and the ether solution was subjected to bicarbonate extraction, and the extract was acidified to get white crystalline solids, *o*-toluic acid (0.012 g; 59%) from *o*-xylene and *p*-toluic acid (0.014 g; 69%) from *p*-xylene. The organic acids were confirmed by comparison of the melting point with that of the authentic sample and its derivatives, and superimposiblity of the NMR spectra with those of the pure samples. The green mass was confirmed as $(PPh_4)_4[VO_4]$. Yield = 60%.

Catalytic oxidations by 1

Oxidation of toluene:

To a methanol solution (5 ml) of the compound **1** (0.01 g; 0.011 mmol), 5 ml of methanol solution of toluene (0.092 g; 0.1 mmol) was added and then 10 ml H_2O_2. The mixture was refluxed for 8–10 h. The solution was cooled and the methanol was evaporated out. The residue was extracted with CH_2Cl_2. The CH_2Cl_2 layer was then again repeatedly extracted with diethyl ether, from where white shinning benzoic acid crystal was obtained by aqueous bicarbonate extraction and further acidification. The remaining ether extract gave toluene. And the catalyst (0.008 g) was obtained from

the dichloromethane layer. Conversion of benzoic acid is 90%.

Oxidation of o-xylene:

To the methanol solution (5 ml) of the compound **1** (0.01 g; 0.011 mmol) was added methanol solution (5 ml) of *o*-xylene (1.06 g; 0.1 mmol) and 10–12 ml of H_2O_2. The mixture was refluxed for 10–12 h. It was cooled, slightly diluted with water and it was then evaporated to make methanol free when white crystals of *o*-toluic acid separated out, conversion was 58.8%. The aqueous part was repeatedly extracted with CH_2Cl_2 which was shaken with diethyl ether to separate the catalyst (0.006 g) and unreacted *o*-xylene obtained from ether layer.

Oxidation of p-xylene:

To the methanol solution (5 ml) of the compound **1** (0.01 g; 0.011 mmol) was added 5 ml of methanol solution of *p*-xylene (1.06 g; 0.1 mmol) and 10–12 ml of H_2O_2. The mixture was refluxed for 10–12 h and *p*-toluic acid was obtained by similar procedure as done in the case of *o*-xylene oxidation. The conversion of *p*-toluic acid was 65.4%. The isolated oxidised products[8] were characterised as before.

Results and discussion

The reaction of V_2O_5 with H_2O_2 was studied in the neutral medium and the yellow orange solution obtained by such a reaction have been found to be sufficiently stable at room temperature. The addition of PPh_4Cl to this solution gave presumably a dimeric oxo-peroxo compound of the type $(PPh_4)_2[V_2O_2(\mu_2\text{-}O)(\mu_2\text{-}O_2)(\eta^2\text{-}O_2)_2]$. Among the three peroxo groups present in the compound, two are probably coordinated in a triangular fashion, one terminal peroxo group per vanadium atom and the remaining peroxo group bridges between the two vanadium centres. The two probable structures of the oxo-peroxo vanadium(VI) compound are given in Fig. 1.

The compound has been characterised by several physiochemical techniques.

The molar conductance data of the compound shows that it is a 2:1 electrolyte[9] as required by their molecular formula.

The oxidation state of vanadium in **1** should be +5, which is corroborated by the observed diamagnetic behaviour of the complexes.
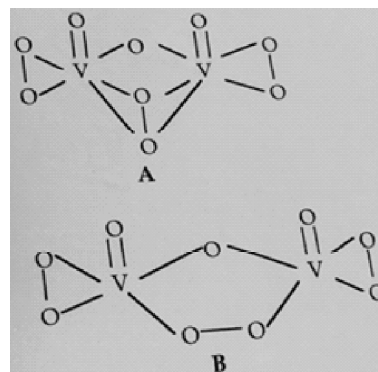

Fig. 1

The infra spectral studies of the isolated complex have been found to be extremely useful in determining the possible structure of the isolated complex.

The strong IR band around 975 cm^{-1} in the spectrum of the oxo peroxo vanadate can be assigned to the ν(V=O) vibration[10], while the strong band at 845 cm^{-1} and the medium intensity band around 815 cm^{-1} are attributable to the ν(O-O)[11] vibration of two different types (terminal and bridging) of coordinated peroxo groups. ν(O-O) vibration for the triangularly bonded peroxo group generally appears at higher wave number than that of bridging peroxo groups and the ν(O-O) vibration in the latter case span a range of 790–844 cm^{-1} with an average value of 810 cm^{-1}. Hence the strong intensity band near 845 cm^{-1} in the compound **1** may be assigned to ν(O-O)[11], vibration (one O_2^{2-} being coordinated per V atom) while the medium intensity band around 810 cm^{-1} can be attributed to the ν(O-O) vibration for the μ-peroxo group, bridging between two vanadium atoms. The medium intensity IR band around 755 cm^{-1} in **1** can be assigned to the ν(V-O-V) asymmetric vibration. The corresponding symmetric band appears at 455 cm^{-1}. The comparatively weak IR band around 610 cm^{-1} and 525 cm^{-1} in **1** can be attributed to the asymmetric and symmetric mode of vanadium and oxygen vibration.

Electronic spectral studies:

The electronic spectra of the dimeric oxoperoxo anionic complex **1** is taken in acetonitrile. The electronic spectra of **1** shows a single band (excluding the bands due to the cation) around 350 nm which can be attributed to O_2^{2-} Pπ* to $V_{d\pi}$ LMCT transition[12].

The thermoanalytical study of **1** is very important in determining the number of peroxo groups coordinated to the metal center.

Thermoanalytical studies:

A derivatographic study of **1** shows loss of O_2 molecule from the peroxo groups exothermally at a temperature range of 100–250°C. This is corroborated by the DTA and TGA curve. The percent weight loss calculated from the TGA curve tallies fairly well with the loss of three peroxo oxygen atoms from the compounds **1**. The PPh_4 salt of the oxoperoxo anion shows one step exothermic loss of O_2 molecule around 270°C. On the other hand, the DTA curve of **1** shows strong exothermic peak around 400°C and this can be attributed to more serious type of decomposition leading to the formation of oxide of vanadium.

Reactivity of the isolated compound

Chemical reactivity of $(PPh_4)_2[V_2O_2(\mu_2\text{-}O)$ $(\mu_2\text{-}O_2)$ $(\eta^2\text{-}O_2)_2]$. Generation of $[VO_4]^{4-}$:

The vanadium complex **1** is found to be capable of transferring its peroxo oxygen to a suitable oxygen acceptor e.g. PPh_3. The peroxo complex of vanadium converts Ph_3P to Ph_3PO under refluxing conditions in polar organic solvent. The oxoperoxo vanadate anion of $[V_2O_2(\mu_2\text{-}O)$ $(O_2)_2$ $(\mu\text{-}O)]^{2-}$ after transferring its peroxo oxygen to PPh_3 is ultimately converted to a product which analysed to $(PPh_4)_4[VO_4]$ presumably contains discrete $[VO_4]^{4-}$ ion.

The molar conductance data of $(PPh_4)_4[VO_4]$ shows that it is a 4:1 electrolyte as required by its molecular formula.

The IR spectrum of $(PPh_4)_4[VO_4]$ shows a single strong band (excluding the bands due to the cation) at 1000 cm^{-1} which is attributed to the $\nu(V=O)$ vibration of the $[VO_4]^{4-}$ tetrahedron.

The UV-Vis spectrum of $(PPh_4)_4[VO_4]$ in solvent acetonitrile shows a broad band near 950 nm ($\varepsilon = 1525$ mol^{-1} cm^{-1}) which can be attributed to the ^2E to $^2T_2$ transition of tetrahedrally coordinated $[VO_4]^{4-}$ ion.

The magnetic susceptibility of $(PPh_4)_4[VO_4]$ is *ca.* 1.85 B.M. and this confirms the oxidation state of vanadium to be +4 in this case.

The electron paramagnetic resonance spectrum of PPh_4 salt of $[VO_4]^{4-}$ ion was found to be similar to that of the MnO_4^{2-}, ReO_4^{2-} and CrO_4^{3-} ions, all of which contain one unpaired electron and consist of a single line observable at $T = 298$ K. The shape and contour of the peak in the $[VO_4]^{4-}$ case is also highly symmetrical with a $<g_s>$ value of 1.91 and this isotropic nature of the ESR signal can be attributed to the regular tetrahedral arrangement of oxygen atoms around the V(IV) center. As the temperature is lowered, the line width as well as the $<g_s>$ value remains almost the same. Thus, the PPh_4 salt of VO_4^{4-} exhibits cubic symmetry (T_d) in their microcrystalline state in the temperature range (298 K to 77 K) studied. Another feature of the ESR spectrum of the V(IV) complex is that ^{51}V hyperfines do not show up.

### Stoichiometric and catalytic reactivity of 1

Aromatic hydrocarbons constitute one of the major groups of basic building blocks of the petrochemical industry. The most important source is the catalytic reforming of naphtha, which affords a mixture of benzene, toluene, ethylbenzene and xylenes, together with C_9 and C_{10} aromatic hydrocarbons to such industrial chemicals as phenols, terephthalic acid and acetone. **1** has been capable of transforming methyl benzenes such as toluene, *o*-xylene and *p*-xylene to benzoic acid, *o*-toluic acid and *p*-toluic acid respectively under refluxing methanol condition, stoichiometrically whereby **1** is converted to **2**. The probable eqs. (1), (2) and (3) governing the reactions are shown below.
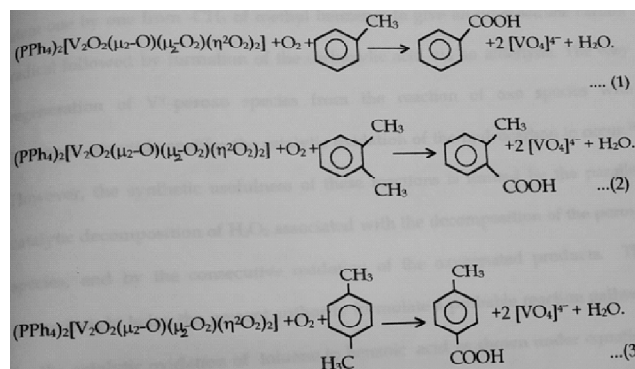
1 though stable in protic solvents, such as methanol, decomposes homolytically in non protic solvents like CH_2Cl_2, MeCN etc., to give O_2 and the corresponding V^V-dioxo complex[14]. The reactivity of V^V-peroxo complex towards hydrocarbons parallels its decomposition rate in dipolar protic sol-

vents. So, a protic solvent, i.e. methanol is used in the reactivity work.

1 also catalytically oxidises the methyl benzene (toluene, *o*- and *p*-xylenes) into the respective carboxylic acids (as mentioned in the stoichiometric oxidations) in presence of hydrogen peroxide and dioxygen. The reactivity of V^V-peroxo complexes may tentatively be attributed to a biradical species(V^{IV}-O-O). The biradical species could abstract a hydrogen atom one by one from -CH_3 of methyl benzenes to give an intermediate carbon radical followed by formation of the carboxylic acid via an aldehyde. The easy regeneration of V^V-peroxo species from the reaction of oxo species with hydrogen peroxide enables the catalytic oxidation of the hydrocarbon to occur[16]. However, the synthetic usefulness of these reactions is limited by the parallel catalytic decomposition of H_2O_2 associated with the decomposition of the peroxo species, and by the consecutive oxidation of the oxygenated products. The above insight helps to formulate a probable reaction pathway for the catalytic oxidation of toluene to benzoic acid as shown under eqs. (4)-(12). So, in the overall process, 2 moles of hydrogen peroxide is consumed.
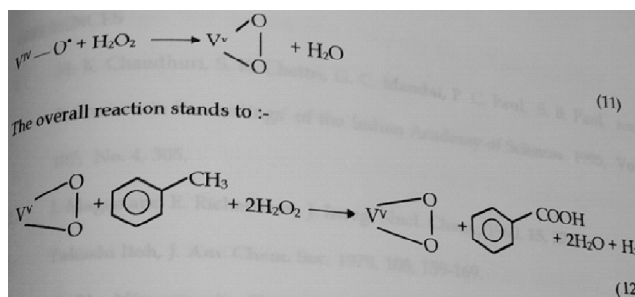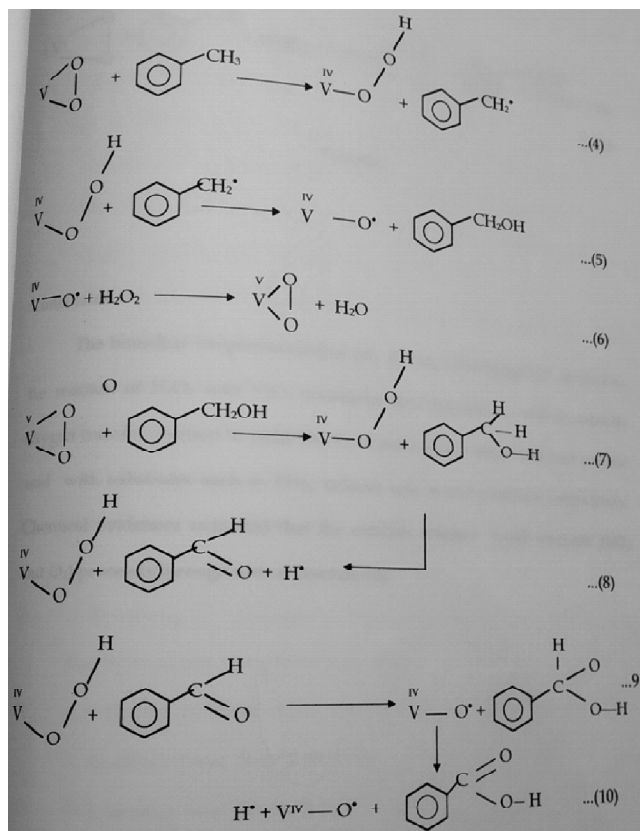
But excess peroxide hinders the overall catalysis process. Since it leads to the decomposition of the catalyst itself. Interestingly, no oxidation occurs if benzoquinone is added in the reaction medium and a 80% yield (as against only 30% without AIBN) is obtained, after only 3 h reflux by using AIBN, azo-bis(isobutyronitrile), indicating that the oxidation proceeds via radical mechanism.

Conclusion

The binuclear oxoperoxovandate(v), $[V_2O_2(\mu_2\text{-O})(\mu_2\text{-}O_2)_2(v_2\text{-}O_2)_2]^{2-}$ formed by the reaction of H_2O_2 with $V_2\text{-}O_5$ undergoes stoichiometric as well as catalytic oxygen transfer reaction to yield Ph_3PO, benzoic acid, *o*-toluic acid and *p*-toluic acid with substrates such as PPh_3, toluene and *o*- and *p*-xylenes respectively. Chemical evidences indicated that the catalytic reaction (with oxidants H_2O_2 and O_2) proceeds through radical mechanism.

Acknowledgement

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